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(54) **MEMBRANE-ELECTRODE ASSEMBLY FOR FUEL CELL AND FUEL CELL USING SAME**

MEMBRAN-ELEKTRODEN-BAUGRUPPE FÜR EINE BRENNSTOFFZELLE UND BRENNSTOFFZELLE DAMIT

ASSEMBLAGE ÉLECTRODE-MEMBRANE POUR PILE À COMBUSTIBLE ET PILE À COMBUSTIBLE UTILISANT CELUI-CI

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Description

Technical Field

[0001] The present invention relates to a membrane-electrode assembly for a fuel cell, in particular relates to an electrode catalyst layer of a membrane-electrode assembly for a fuel cell.

Background

[0002] Recently, in response to social needs or movement with the background of energy and environmental issues, a fuel cell has been noticed as a vehicle drive source and a stationary power source. A fuel cell is classified into various types based on electrolyte types or electrode types, which are represented by an alkali type, a phosphoric acid type, a fused carbonate salt type, a solid electrolyte type and a solid polymer type. Among these, because of operability at low temperature (usually not higher than 100°C), a proton-exchange membrane fuel cell (PEFC) has been noticed and development and practical applications thereof have recently been progressing as a source of power for a low pollution type automobile (JP-A-2004-79457).

[0003] Composition of PEFC, generally, has such structure that a membrane-electrode assembly (MEA) is sandwiched by separators. Generally, MEA has structure laminated with a gas diffusion layer, a cathode catalyst layer, a solid polymer electrolyte membrane, an anode catalyst layer and a gas diffusion layer.

[0004] In MEA, the following electrochemical reaction proceeds. First, hydrogen contained in fuel gas supplied to an anode (fuel electrode) side is converted to protons and electrons by oxidation with a catalyst. Then, resultant protons pass through a polymer electrolyte contained in the anode side catalyst layer, and further through a solid polymer electrolyte membrane contacting with the anode side catalyst layer, and reach the cathode (air electrode) side catalyst layer. In addition, electrons generated at the anode side catalyst layer pass through a conductive carrier composing the anode side catalyst layer, and further the gas diffusion layer contacting with the anode side catalyst layer at a different side of the solid polymer electrolyte membrane, the gas separator and an external circuit, and reach the cathode side catalyst layer. Then, protons and electrons reached the cathode side catalyst layer react with oxygen contained in oxidizing agent gas supplied to the cathode side catalyst layer, and generate water. In a fuel cell, electricity can be taken out through the aforementioned electrochemical reaction.

[0005] As applications of PEFC, a vehicle drive source or a stationary power source has been studied. To be suitable to such applications, durability for a long period is required. In particular, use as a vehicle drive source requires no lowering of cell characteristics caused by frequent start-stop operation.

[0006] In particular, in an electrode catalyst layer containing a catalyst comprising platinum or a platinum alloy, conductive carbon material supporting a catalyst, and a proton conductive polymer electrolyte, repeated start-stop operation easily generates corrosion of the conductive carbon material or degradation of the polymer electrolyte by decomposition, and tends to reduce gas diffusion property and drainage property of the electrode, increase concentration over-voltage and lower cell characteristics.

[0007] Therefore, many attempts have been taken to improve corrosion resistance of conductive carbon material in the past. For example, JP-A-05-129023 and JP-A-2005-26174 have disclosed conductive carbon material having improved corrosion resistance by controlling crystallinity of carbon by means of heat treatment.

US 2002/0064699 A1 discloses a membrane-electrode assembly for a fuel cell which comprises cathode catalyst layer containing a cathode catalyst comprising platinum or a platinum alloy, a conductive carbon material supporting said cathode catalyst, and a proton conductive polymer electrolyte; a solid polymer electrolyte membrane; and an anode catalyst layer containing, an anode catalyst, a conductive carbon material supporting said anode catalyst, and a proton conductive polymer electrolyte. The fuel cell shows enhanced power-generating performance.

Disclosure of the Invention:

[0008] PEFC is required to show, as described above, high power generation performance over a long period. However, there have been some possibilities that a conventional membrane-electrode assembly can not provide sufficient power generation performance, even by conductive carbon material having improved corrosion resistance by heat treatment, as described in JP-A-05-129023 and JP-A-2005-26174, and the like.

[0009] One of the causes to lower power generation performance of a membrane-electrode assembly by repeated start-stop operation is considered to be residual hydrogen at an anode side in stopping. Hydrogen is supplied to an anode side as fuel, and when operation of a membrane-electrode assembly is stopped, residual hydrogen at an anode side is purged by supplying gas such as air to an anode side. However, when hydrogen is not completely purged and certain amount of hydrogen is left at an anode side, a local cell is formed at an anode side in starting operation, which makes a cathode side exposed in high voltage state. Consequently, oxygen is generated by electrolysis of water at platinum supported as a catalyst, resulting in oxidative corrosion of carbon material by a reaction of $C + O_2 \rightarrow CO_2$. Corrosion of carbon material results in deformation and deterioration of an electrode catalyst layer at a membrane-electrode assembly, increase in concentration over-voltage, and serious performance deterioration of PEFC. In addition, in a membrane-electrode assembly, elution of platinum to a solid polymer electrolyte membrane or decomposition of a polymer electrolyte is also induced by repeated start-stop operation in a membrane-electrode assembly, which also becomes a cause of performance deterioration of PEFC.

[0010] Therefore, an object of the present invention is to improve durability of a membrane-electrode assembly for a fuel cell for start-stop operation.

[0011] The present inventor has intensively studied, in view of the problems, and has clarified that durability of a cathode catalyst layer for repeated start-stop operation of a membrane-electrode assembly for a fuel cell can be enhanced by making an anode catalyst layer thinner relative to a cathode catalyst layer.

[0012] Namely, the problems can be solved by the following (1) to (3).

[0013]

(1) A membrane-electrode assembly for a fuel cell having:

a cathode catalyst layer containing a cathode catalyst comprising platinum or a platinum alloy, a conductive carbon material supporting said cathode catalyst, and a proton conductive polymer electrolyte;
a solid polymer electrolyte membrane; and
an anode catalyst layer containing an anode catalyst, a conductive carbon material supporting said anode catalyst, and a proton conductive polymer electrolyte;
wherein average thickness of said anode catalyst layer (Ya) is smaller than average thickness of said cathode catalyst layer (Yc), and wherein said conductive carbon material of the cathode catalyst layer comprises graphitized carbon black.

(2) A proton-exchange membrane fuel cell using the membrane-electrode assembly for a fuel cell set forth in (1).
(3) A vehicle mounted with the proton-exchange membrane fuel cell set forth in (2).

Best Embodiment for Carrying Out the Invention:

[0014] Embodiments of the present invention are explained in detail below.

[0015] The first aspect of the present invention is:

A membrane-electrode assembly for a fuel cell having:

a cathode catalyst layer containing a cathode catalyst comprising platinum or a platinum alloy, conductive carbon material supporting the cathode catalyst, and a proton conductive polymer electrolyte;
a solid polymer electrolyte membrane; and
an anode catalyst layer containing an anode catalyst, conductive carbon material supporting the anode catalyst, and a proton conductive polymer electrolyte;

wherein average thickness of the anode catalyst layer (Ya) is smaller than average thickness of the cathode catalyst layer (Yc), and wherein said conductive carbon material of the cathode catalyst layer comprises graphitized carbon black.

[0016] In the membrane-electrode assembly for a fuel cell of the present invention, average thickness of the anode catalyst layer (Ya) is designed to be smaller than average thickness of the cathode catalyst layer (Yc). By this design, hydrogen remaining at the anode side in stopping operation is efficiently purged with other gas. As a result, formation of a local cell at the anode side in starting operation is suppressed, and deterioration of the membrane-electrode assembly is prevented.

[0017] In addition, when the anode catalyst layer is thin, water content of the anode catalyst layer tends to be lowered in purging with gas such as air for replacing hydrogen at the anode side in stopping operation. Namely, the anode catalyst layer tends to be dried easily. Consequently, as compensation of water content lowered at the anode catalyst layer, water migration occurs from the solid polymer electrolyte membrane having relatively high water content. At the same time, water migration occurs from the cathode catalyst layer to the solid polymer electrolyte membrane, which decreases water content of the cathode catalyst layer. Oxygen does not generate if water is not present at the vicinity of a platinum catalyst, even when the cathode catalyst layer is exposed to high voltage in starting operation. Therefore, carbon corrosion in start-stop operation can be suppressed.

[0018] However, the mechanism on composition and the effect of the present invention is only estimation, and technical scope of the present invention should not be limited to embodiments utilizing the mechanism.

[0019] As described above, in the membrane-electrode assembly of the present invention, average thickness of the anode catalyst layer (Ya) is designed to be smaller than average thickness of the cathode catalyst layer (Yc) Specifically, Ya and Yc preferably satisfy the relation of Ya/Yc=0.01 to 0.9, more preferably Ya/Yc=0.03 to 0.86. By controlling thickness of the catalyst layer to satisfy these relations, the membrane-electrode assembly having excellent durability can be obtained.

[0020] Average thickness of the anode catalyst layer (Ya) is preferably 0.3 to 10 μm, more preferably 0.3 to 8 μm, and particularly preferably 2 to 6 μm. In addition, average thickness of the cathode catalyst layer (Yc) is preferably 7 to 20 μm, and more preferably 7 to 15 μm. By adopting these ranges, carbon corrosion or platinum elution in start-stop operation or in load variation can effectively be suppressed. A thinner catalyst layer provides more excellent gas diffusion property and permeability, along with drainage of humidification water and generated water, however, a too thin catalyst layer makes durability retention difficult, therefore, preferable thickness may be determined by taking balance thereof.

[0021] In this connection, in the present invention, thickness of each catalyst layer at the anode and the cathode is obtained by measuring thickness of the catalyst layer at 20 to 50 points, in an electron micrograph (magnification: 3000 times) of the cross-section of the catalyst layer taken under condition of a acceleration voltage of 3 kV, using a scanning electron microscope, and averaged value thereof is used.

[0022] Then, composition material of PEFC of the present invention is explained.

[0023] The cathode catalyst layer contains a catalyst comprising platinum or a platinum alloy, conductive carbon material supporting the cathode catalyst, and a proton conductive polymer electrolyte. In the cathode catalyst layer, the cathode catalyst preferably is supported on the conductive carbon material, and used as the cathode electrode catalyst.

[0024] The cathode catalyst is material for fulfilling a role to promote a reaction at the cathode side (air electrode) of the membrane-electrode assembly, and at least platinum or a platinum alloy is used. As the platinum alloy, although not especially limited, an alloy between platinum and iridium or an alloy between platinum and rhodium preferably is included due to providing high catalytic activity. In addition to the above, as the platinum alloy, an alloy between at least one kind of base metal selected from chromium, manganese, iron, cobalt and nickel, and platinum
preferably is included, aiming at improvement of heat resistance, poisoning resistance against carbon monoxide, and the like. Mixing ratio of the platinum and the base metal in the platinum alloy preferably is 1/1 to 5/1 in mass ratio (platinum/base metal), in particular, 2/1 to 4/1. By adopting the ratio, a cathode catalyst having poisoning resistance, corrosion resistance, and the like while maintaining high catalytic activity can be obtained.

[0025] Average particle diameter of the cathode catalyst is not especially limited, and is preferably 1 to 20 nm, and more preferably 2 to 10 nm. Catalyst particles are predicted to have also more improved catalytic activity with smaller average particle diameter due to having increased specific surface area, however, in practice, catalytic activity comparable to increment in specific surface area tends not to be obtained, even if catalyst particle diameter is made supremely small.

[0026] In this connection, average particle diameter of the cathode catalyst and the anode catalyst represents average value of crystal particle diameter determined by half bandwidth of the diffraction peak of the cathode catalyst or the anode catalyst in X-ray diffraction, or by particle diameter of the cathode catalyst or the anode catalyst examined by transmission electron microscope image.

[0027] The conductive carbon material is carbon material having function as a carrier of the cathode catalyst and conductivity, and may also be called as conductive carbon. Electron transfer at a moiety where an electrode reaction practically proceeds is carried out through the conductive carbon material. As the conductive carbon material of the cathode catalyst layer, graphitized carbon black is used. Usual carbon black, although having higher hydrophobicity compared with that of an oxide, and the like, has hydrophylicity due to presence of small amount of functional groups such as a hydroxyl group or a carboxyl group at the surface. On the other hand, graphitized carbon black, due to having decreased amount of a hydrophilic functional group, improves hydrophobicity. Use of carbon black with improved hydrophobicity is capable of improving drainage of the electrode catalyst layer, which in turn improves cell performance of PEFC.

[0028] As the carbon black, although not especially limited as long as it is a general one conventionally used, channel black, furnace black, thermal black, Ketjenblack, Black Pearls, and the like preferably is included. In addition, a commercially available one can be used as the carbon black, including oil furnace black such as Vulcan XC-72, Vulcan P, Black Pearls 880, Black Pearls 1100, Black Pearls 1300 and Black Pearls 2000, REGAL 400 manufactured from Cabot Co., Ltd., Ketjenblack EC manufactured from Lion Corp., #3150 and #3250 manufactured from Mitsubishi Chemical Corp. and the like; and acetylene black such as Denka Black manufactured from Denki Kagaku Kogyo Kabushiki Kaisyha; and the like.

[0029] The graphitization treatment is not especially limited as long as it is one generally used conventionally such as heat treatment. The heat treatment preferably is carried out under inert gas atmosphere such as nitrogen, argon and helium. In addition heat treatment temperature and heat treatment time may be determined, as appropriate, so that the resultant graphitized carbon black has desired BET surface area, because of dependency on carbon material to be used, and may be carried out at 2000 to 3000°C for about 5 to 20 hours.

[0030] Graphitization degree of the graphitized carbon black may be not lower than 75%, and preferably 80 to 95%. By adopting this range, functional groups at the surface of carbon black can be reduced, which can not only secure water-repellent property but also improve corrosion resistance and electric conductivity by change in crystal structure.

[0031] As the graphitized carbon black, one having a true density of 1.80 to 2.11 g/cm^3, and lattice spacing, d_{002}, of 3.36 to 3.55 Å preferably is used.

[0032] In the present invention, lattice spacing, d_{002}, of the graphitized carbon black is plane distance of a hexagonal network plane based on graphite structure of carbon black, and represents average value of half interlayer distance of lattice constant in the "c" axis direction, which is a perpendicular direction of the hexagonal network plane.

[0033] In the graphitized carbon black obtained by some way such as heat treatment, a graphitized layer composed of 3D crystal lattice similar to graphite structure is formed at the surface, and fine inter-crystal lattice space moiety decreases with progress of graphitization, and thus crystal structure of the conductive carbon material approaches to crystal structure of graphite. In consideration of corrosion resistance in addition to water-repellent property, crystallinity of conductive carbon material to be used preferably is as high as possible.

[0034] When a true density of the graphitized carbon black is below 1.80 g/cm^3 and lattice spacing, d_{002}, is over 3.55 Å, in many cases graphite structure may not sufficiently be developed, and high corrosion resistance and electron conductivity could not be obtained. In addition, when a true density is over 2.11 g/cm^3 and lattice spacing, d_{002}, is below 3.36 Å, in many cases graphite structure may excessively be developed, and sufficient specific surface area could not be obtained.

[0035] Therefore, as the graphitized carbon black, one having a true density of 1.80 to 2.11 g/cm^3, and a lattice spacing, d_{002}, of 3.36 to 3.55 preferably is used, and more preferably one with a true density of 1.90 to 2.11 g/cm^3, and a lattice spacing, d_{002}, of 3.38 to 3.53 Å, and particularly preferably one with a true density of 1.90 to 2.11 g/cm^3, and a lattice spacing, d_{002}, of 3.40 to 3.51 Å is used

[0036] In this connection, in the present invention, true density is a value measured by a vapor phase replacement method using helium, and lattice spacing, d_{002}, is a value measured by Gakushin method (Michio Inagaki, "Carbon" No. 36, 25-34 (1963)) using an X-ray diffraction method.

[0037] In addition, as the graphitized carbon black, one having an electric conductivity of 50 to 1000 S/cm, preferably 100 to 1000 S/cm is used.

[0038] The graphitized carbon black is required not only to support the cathode catalyst but also have function as a power collecting body to take out electrons to an external circuit, or take in electrons from an external circuit, to be used as the electrode catalyst of a high performance fuel cell. An electric conductivity of the graphitized carbon black of below 50 S/cm may incur high internal resistance of a fuel cell, and lower cell performance, while an electric conductivity of over 1000 S/cm may promote crystallization of carbon black and decrease BET surface area.

[0039] In the present invention, electric conductivity of the graphitized carbon black is a value measured at 25°C after compression molding the graphitized carbon black under 14 to 140 MPa similarly by a usual method, and then heat treatment at 1000°C under nitrogen atmosphere.

[0040] In the present invention, the graphitized carbon black preferably contains the graphitized carbon black (A) having a BET surface area of preferably not smaller than 100 m^2/g, more preferably 100 to 300 m^2/g and particularly preferably 120 to 250 m^2/g. By using the graphitized carbon black (A), the cathode electrode catalyst excellent in catalytic activity can be obtained, due to having not only excellent drainage but also corrosion resistance, and further good dispersion of the cathode catalyst supported thereon.

[0041] Amount of the supported catalyst in the graphitized carbon black (A) is not especially limited. The amount of the supported catalyst may be determined, as appropriate, so that desired power generation characteristics is obtained, by kind of the cathode catalyst, performance of the membrane-electrode assembly and kind of the graphitized carbon black (A). Specifically, when the graphitized carbon black (A) supporting the cathode catalyst is used as the cathode electrode catalyst (C), the amount of the supported cathode catalyst in the cathode electrode catalyst (C) based on total mass of the cathode electrode catalyst (C) is preferably 20 to 80% by mass, more preferably 40 to 60% by mass. The amount of the supported catalyst to be in this range is capable of suppressing for oxygen generating at the vicinity of the platinum catalyst to contact with carbon surface, and thus oxidative corrosion thereof, when exposed to high voltage.

[0042] As the conductive carbon material in the cathode catalyst layer, graphitized carbon black (B) having a BET surface area of preferably smaller than 100 m^2/g, and more preferably 80 to 100 m^2/g preferably is contained in addition to the graphitized carbon black (A). The graphitized carbon black (B) is excellent not only water-repellent property but also, in particular, corrosion resistance. Therefore, use of the graphitized carbon black (A) and the graphitized carbon black (B) as carriers of the cathode catalyst is capable of providing high catalytic activity by the graphitized carbon black (A), and further improved corrosion resistance by the graphitized carbon black (B), resulting in the membrane-electrode assembly with excellent power generation performance and durability.

[0043] Amount of the supported catalyst by the graphitized carbon black (B) is not especially limited and specifically, when the graphitized carbon black (B) supporting the cathode catalyst is used as the cathode electrode catalyst (D), the amount of the supported cathode catalyst in the cathode electrode catalyst (D) is preferably 10 to 50% by mass, more preferably 10 to 30% by mass based on total mass of the cathode electrode catalyst (D). The amount of the supported catalyst to be in this range is capable of providing the cathode catalyst having both corrosion resistance and catalytic activity.

[0044] In the case when the graphitized carbon black (A) and the graphitized carbon black (B) are used as conductive carbon material which is a carrier of the cathode electrode catalyst, to satisfy both durability and catalytic performance of the cathode catalyst, along with to reduce decreasing degree of catalytic activity over time, the cathode catalyst to be supported on the graphitized carbon black (A) and the graphitized carbon black (B) is preferably supported to each after adjustment of average particle diameter.

[0045] Specifically, average particle diameter of the cathode catalyst on the graphitized carbon black (A) is 2 to 8 nm, and preferably is 3 to 6 nm. The average particle diameter below 2 nm may not provide high catalytic activity at the initial stage of power generation, and the average particle diameter over 8 nm provides excessively large particle diameter of the cathode catalyst supported, which may result in too small activated surface area and oppositely reduce catalytic activity. In addition, average particle diameter of the cathode catalyst to be supported on the graphitized carbon black (B) is 4 to 10 nm, and preferably is 4 to 8 nm. The average particle diameter below 4 nm may not sufficiently suppress reduction over time of catalytic activity, while over 8 nm is too large as particle diameter of the cathode catalyst supported and reduces activated surface area which may oppositely reduce catalytic activity.

[0046] In the cathode catalyst layer, to further improve durability and power generation performance of the membrane-electrode assembly, the cathode electrode catalyst (C) to be composed of the cathode catalyst supported on the graphitized carbon black (A), and the cathode electrode catalyst (D) to be composed of the cathode catalyst supported on the graphitized carbon black (B) preferably is mixed by specified ratio.

[0047] Namely, in the cathode catalyst layer, the cathode electrode catalyst (C) and the cathode electrode catalyst (D) is mixed in preferably not smaller than 60/40 as mass ratio (C)/(D), more preferably 60/40 to 99/1, particularly preferably 80/20 to 99/1, and further preferably 85/15 to 95/5. The mixing ratio of the cathode electrode catalyst (C) and the cathode electrode catalyst (C) below 60/40, as mass ratio (C)/(D), could lower power generation performance, and therefore the ratio preferably is within the above range.

[0048] In the cathode catalyst layer, water generating with progress of an electrode reaction is labile to transfer with flow of fuel gas supplied. Under the operation condition of high current density or high humidification, deterioration of the cathode electrode catalyst tends to be serious from upstream toward downstream of a gas flow channel in the cathode catalyst layer, caused by much amount of generating water retained at the vicinity of a gas discharge portion of the cathode catalyst layer, which inhibits progress of the electrode reaction. Therefore, in the cathode catalyst layer, when the cathode electrode catalyst (C) and the cathode electrode catalyst (D) are contained, composition of the cathode electrode catalyst preferably is optimized from upstream toward downstream of the gas flow channel.

[0049] Namely, at the downstream side of the gas flow channel of the cathode catalyst layer, mass ratio (C)/(D) of the cathode electrode catalyst (C) and the cathode electrode catalyst (D) preferably is smaller than mass ratio (C)/(D) of the cathode electrode catalyst (C) and the cathode electrode catalyst (D) at the upstream side of the gas flow channel of the cathode catalyst layer.

[0050] Specifically, ratio of mass ratio (C) / (D) (=R_{up}) between the cathode electrode catalyst (C) and the cathode electrode catalyst (D) at the upstream side of the gas flow channel of said cathode catalyst layer, and mass ratio (C)/(D)(=R_{down}) between the cathode electrode catalyst (C) and the cathode electrode catalyst (D) at the downstream side of the gas flow channel of said cathode catalyst layer, i.e. R_{up}/R_{down} preferably is not smaller than 1/1, more preferably 2/1 to 9/1, and particularly preferably 3/1 to 6/1.

[0051] By adopting such range, the cathode catalyst layer without bias in the electrode reaction inside the cathode catalyst layer, and with desired performance maintained for a long period can be prepared.

[0052] In this connection, the upstream side of gas flow channel of the cathode catalyst layer is defined as the vicinity of entrance and the downstream side of gas flow channel of the cathode catalyst layer is defined as the vicinity of exit portions of fuel gas. Specific range thereof and the like may be determined in consideration of characteristics of the resulting catalyst layer.

[0053] Further described but not part of the present invention is the use of hydrophobicity-treated carbon black using a fluorine compound which may be used as the conductive carbon material of the cathode catalyst layer. By using such carbon black, hydrophobicity of the cathode catalyst layer can further be improved. Use amount of the hydrophobicity-treated carbon black using a fluorine compound preferably is 1 to 20% by mass based on total mass of the conductive carbon material of the cathode catalyst layer. By formulation of the amount within this range, high power generation performance can be expressed from the initial stage to after long period of operation, and covering from low current density to high current density, and improved durability and long life property can be attained. In this connection, as an example of hydrophobized treatment, a method for treating carbon black with polytetrafluoroethylene is included.

[0054] In addition, also not forming part of the present invention is the use of a carbon nanotube, a carbon nanofiber or a carbon nanohorn which is used as the conductive carbon material of the cathode catalyst layer. By the addition of a carbon nanotube, a carbon nanofiber or a carbon nanohorn having higher graphitization degree than carbon black, hydrophobicity in the cathode catalyst layer can be improved and destruction of three phase structure caused by deterioration can be suppressed. Depending on the case, 2 or 3 kinds of a carbon nanotube, a carbon nanofiber or a carbon nanohorn may be used in combination. Use amount of a carbon nanotube, a carbon nanofiber or a carbon nanohorn is 1 to 20% by mass based on total mass of the conductive carbon material of the cathode catalyst layer. By formulation of the amount within this range, high power generation performance can be expressed from the initial stage to after long period of operation, and covering from low current density to high current density, and therefore improved durability and long life property can be attained.

[0055] A proton conductive polymer electrolyte used in the cathode catalyst layer and the anode catalyst layer fulfills a role to enhance mobility of protons transferring between the cathode (air electrode) and the anode (fuel electrode) in power generation of PEFC.

[0056] A polymer electrolyte is not especially limited as long as it is one generally used in the catalyst layer. Specifically, polymer electrolytes such as a perfluorocarbon polymer having a sulfonic acid group, for example Nafion™ (manufactured from DuPont Co., Ltd.); a hydrocarbon based polymer compound doped with an inorganic acid such as phosphoric acid; an organic/inorganic hybrid polymer substituted with a proton conductive functional group at a part thereof; a proton conductor composed of polymer matrix impregnated with a phosphoric acid solution or a sulfuric acid solution; and the like are included.

[0057] A solid polymer electrolyte membrane is an ion conductive membrane present between the cathode catalyst layer and the anode catalyst layer. The solid polymer electrolyte membrane is not especially limited, and a membrane composed of a proton conductive electrolyte similar to one used in the electrode catalyst layer may be used. For example, a solid polymer electrolyte membrane generally available on the market, such as a perfluorosulfonic acid membrane represented by various Nafion™ manufactured by DuPont Co., Ltd. or Flemion™, can be used. A membrane made of a polymeric microporous membrane impregnated with a liquid electrolyte, a membrane made of a porous body filled with a polymer electrolyte, and the like may be used. A polymer electrolyte used in the solid polymer electrolyte membrane and a proton conductive electrolyte used in the electrode catalyst layer may be the same or different, however, the same one preferably is used in view of improvement of adhesion between the electrode catalyst layer and the solid polymer electrolyte membrane.

[0058] Thickness of the solid polymer electrolyte membrane may be determined, as appropriate, in consideration of characteristics of the resulting MEA, however, preferably is not too thin in view of strength in membrane production or durability in usage, and preferably is not too thick in view of output characteristics in usage. Specifically, thickness of the solid polymer electrolyte membrane is preferably 5 to 300 μm, more preferably 10 to 200 μm and particularly preferably 15 to 100 μm.

[0059] The anode catalyst layer contains the anode catalyst, the conductive carbon material for supporting the anode catalyst, and the proton conductive polymer electrolyte.

[0060] The anode catalyst is material fulfilling a role to promote a reaction at the anode side (fuel electrode) of PEFC. Kind of the anode catalyst is not especially limited as long as capable of providing action as the anode catalyst. Platinum or a platinum alloy or the other catalyst may be used, similarly as the cathode catalyst. For example, a catalyst selected from a group consisting of a metal such as platinum, ruthenium, iridium, rhodium, palladium, osmium, tungsten, lead, iron, chromium, cobalt, nickel, manganese, vanadium, molybdenum, gallium and aluminum, and an alloy thereof may be used. Two or more kinds thereof may be used in combination.

[0061] The conductive carbon material of the anode catalyst layer is not especially limited, and preferably carbon black, more preferably graphitized carbon black is used. In the anode catalyst layer, carbon corrosion generates less than in the cathode catalyst layer, even if not graphitized carbon black is used, and high power generation performance, improved durability and long life property can be attained from the initial stage to long period of operation, along with covering from low current density to high current density. Graphitized carbon black improves hydrophobicity due to having decreased amount of hydrophilic functional groups. When carbon black with improved hydrophobicity is used, water content in the anode catalyst layer tends to be decreased, namely, tends to be easily dried, during air purging operation of the anode catalyst layer in stop operation of PEFC.

[0062] The amount of supported catalyst in the conductive carbon material in the anode catalyst layer is not especially limited, and may be determined so that desired power generation characteristics can be obtained, by kind of the anode catalyst, performance of the membrane-electrode assembly, kind of the conductive carbon material, and the like. For example, when the conductive carbon material supporting the anode catalyst is used as the anode electrode catalyst, the amount of the supported anode catalyst in the anode electrode catalyst preferably is 30 to 70% by mass based on total amount of the anode electrode catalyst. Use of the amount of the supported catalyst within this range improves utilization ratio of platinum, which makes possible the anode catalyst layer thinner.

[0063] As fundamental composition of the membrane-electrode assembly of the present invention, such a composition preferably is included that the cathode catalyst layer, the solid polymer electrolyte membrane and the anode catalyst layer are arranged in this order. As a more preferable composition of the membrane-electrode assembly, a gas diffusion layer preferably is arranged at the exterior side of either of the cathode catalyst layer and the anode catalyst layer, and the gas diffusion layer more preferably is arranged at the exterior sides of both of the cathode catalyst layer and the anode catalyst layer. By adopting the above composition, gas supplied from outside can more uniformly be supplied to the electrode catalyst layer, and power generation performance of the membrane-electrode assembly can further be improved.

[0064] Composition material of the gas diffusion layer is not especially limited. For example, conductive and porous sheet-like material, such as carbon-based fabric, paper-like material obtained by paper making, felt, nonwoven fabric are included. In more specifically, carbon paper, carbon cloth, carbon nonwoven fabric, and the like are used. Water-repellent treated carbon paper preferably is used.

[0065] As water-repellent treated sheet-like material preferably used in the gas diffusion layer such as water-repellent treated carbon paper, sheet-like material containing a water repellent agent is included. As the water repellent agent, fluorine-based polymeric material such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyhexafluoropropylene, a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP); polypropylene, polyethylene, and the like are preferably included.

[0066] As the gas diffusion layer, carbon paper with a thickness of not thicker than 400 μm, or water-repellent treated carbon paper preferably is used, and it may be determined, as appropriate, in consideration of characteristics of the resultant gas diffusion layer. In view of water-repellent property of the gas diffusion layer, the gas diffusion layer with a thickness of not thicker than 200 μm more preferably is used. The lower limit of thickness of the gas diffusion layer is not especially limited, however, a too thin layer may not provide sufficient mechanical strength, and therefore a thickness not thinner than 100μm is desirable.

[0067] In addition, to prevent flooding in the membrane-electrode assembly, a mil layer may be arranged between the gas diffusion layer, and the cathode catalyst layer and the anode catalyst layer. The mil layer represents a mixture layer composed of carbon and a water repellent fluorocarbon resin such as polytetrafluoroethylene, formed at the surface of the gas diffusion layer.

[0068] The second aspect of the present invention is a proton-exchange membrane fuel cell (PEFC) using the membrane-electrode assembly for a fuel cell of the first aspect of the present invention. In PEFC of the present invention, the catalyst layer is hard to be deteriorated in the membrane-electrode assembly and is excellent in durability. Namely, in PEFC of the present invention, voltage reduction is little even after PEFC is used for a long period. Such characteristics are particularly useful in applications requiring durability over a long period. Such applications include a vehicle such as an automobile. PEFC of the present invention, due to maintaining power generation characteristics over a long period, is capable of attaining longer lifetime or value improvement of vehicle mounted with PEFC of the present invention. PEFC of the present invention preferably is used as various power sources, and use as a power source of a vehicle particularly be preferable.

[0069] Composition of PEFC is not especially limited, and conventionally well-known technology may be utilized, as appropriate, and generally, has structure that MEAs are sandwiched by separators. Specifically, such composition is included wherein the separator, the gas diffusion layer, the cathode catalyst layer, the solid polymer electrolyte membrane, the anode catalyst layer, the gas diffusion layer and the separator are arranged in this order. However, the present invention should not be limited to such fundamental composition, and the present invention is applicable to also PEFC having other composition.

[0070] Material of the separator is not especially limited, and well-known ones such as a carbon-based separator such as fine carbon graphite or a carbon plate, a metal-based separator such as a stainless steel-based separator, and the like can be used. Thickness or size of the separator, shape of a flow channel, and the like are not especially limited, and may be determined, as appropriate, in consideration of output characteristics of the resultant fuel cell.

[0071] Furthermore, to obtain desired voltage of a fuel cell, and the like, a plurality of MEAs may be laminated via separators in series to form a stack. Shape of a fuel cell and the like are not especially limited, and may be determined, as appropriate, so that desired voltage and the like can be obtained.

Example

Working Example 1

[0072]

1. Preparation of an anode electrode catalyst

As conductive carbon material, 4.0 g of carbon black (Ketjenblack™ EC produced from Ketjen Black International Co., Ltd.; BET surface area=800 m^2/g) was prepared, and 400 g of an aqueous solution of dinitrodiamine platinum (a Pt concentration of 1.0%) was added thereto and stirred for 1 hr. Further, 50 g of methanol was added as a reducing agent and stirred for 1 hr. Subsequently, the solution was warmed to 80°C taking 30 minutes, followed by stirring at 80°C for 6 hrs and cooling to room temperature taking 1 hr. The precipitate was filtered, and then the resultant solid substance was dried at 85°C for 12 hrs under reduced pressure, and crushed in a mortar to yield an anode electrode catalyst (an average particle diameter of Pt particles of 2.6 nm, and a Pt supporting concentration of 50% by mass).

2. Preparation of a cathode electrode catalyst

By graphitization treatment of carbon black (Ketjenblack™ EC produced from Ketjen Black International Co., Ltd.) at 2700°C for 10 hours, graphitized carbon black (graphitized Ketjenblack™ EC; BET surface area=130 m^2/g, true density=1.93 g/cm^3, lattice spacing, d_{002}, =3.51 Å, electric conductivity=2005/cm) was yielded. To 4.0 g of the graphitized Ketjenblack, 400 g of an aqueous solution of dinitrodiamine platinum (a Pt concentration of 1.0%) was added and stirred for 1 hr. Further, 50 g of formic acid was mixed as a reducing agent and stirred for 1 hr. Subsequently, the solution was warmed to 40°C taking 30 minutes, followed by stirring at 40°C for 6 hrs, warming to 60°C taking 30 minutes, further stirring at 60°C for 6 hrs and cooling to room temperature taking 1 hr. The precipitate was filtered, and then the resultant solid substance was dried at 85°C for 12 hrs under reduced pressure, and crushed in a mortar to yield a cathode electrode catalyst (an average particle diameter of Pt particles of 4.8 nm, and a Pt supporting concentration of 50% by mass).

3. Preparation of an anode catalyst layer

Purified water of 5 times mass based on mass of the anode electrode catalyst was added, and subjected to defoaming operation under reduced pressure for 5 minutes. To this solution, 0.5 times mass of n-propyl alcohol was added, and further a solution containing a proton conductive polymer electrolyte (containing 20% by weight of Nafion™ produced from DuPont Co., Ltd.) was added. As content of the polymer electrolyte in the solution, one having mass ratio of solid content to the mass of carbon of the anode electrode catalyst, Carbobn/Ionomer =1.0/0.9, was used. The resultant mixture slurry was sufficiently dispersed by an ultrasonic homogenizer and subjected to defoaming operation under reduced pressure to yield catalyst slurry. This catalyst slurry was printed in the amount responsive to desired thickness, at the one surface of a polytetrafluoroethylene sheet by a screen printing method, which was then dried at 60°C for 24 hours. Size of the anode catalyst layer to be formed was set to be 5 cm × 5 cm. In addition, the coating layer on the polytetrafluoroethylene sheet was adjusted so that a Pt amount of 0.05 mg/cm^2 is obtained.

4. Preparation of a cathode catalyst layer

Purified water of 5 times mass based on mass of the cathode electrode catalyst was added, and subjected to defoaming operation under reduced pressure for 5 minutes. To this solution, 0.5 times mass of n-propyl alcohol was added, and further a solution containing a proton conductive polymer electrolyte (containing 20% by weight of Nafion™ produced from DuPont Co., Ltd.) was added. As content of the polymer electrolyte in the solution, one having mass ratio of solid content to the mass of carbon of the cathode electrode catalyst, Carbobn/Ionomer =1.0/0.9, was used.

The resultant mixture slurry was sufficiently dispersed by an ultrasonic homogenizer and subjected to defoaming operation under reduced pressure to yield catalyst slurry. This catalyst slurry was printed in the amount responsive to desired thickness, at the one surface of a polytetrafluoroethylene sheet by a screen printing method, which was then dried at 60°C for 24 hours. Size of the cathode catalyst layer to be formed was set to be 5 cm × 5 cm. In addition, the coating layer on the polytetrafluoroethylene sheet was adjusted so that a Pt amount of 0.35 mg/cm^2 is obtained.

5. Preparation of membrane-electrode assembly (MEA)

Nafion™ 111 (a membrane thickness of 25 μm) as a solid polymer electrolyte membrane, and the electrode catalyst layer, formed on the polytetrafluoroethylene sheet in advance, were laminated together. In this procedure, the anode catalyst layer, the solid polymer electrolyte membrane and the cathode catalyst layer were laminated in this order. Subsequently, the laminated substance was subjected to hot pressing at 130°C for 10 minutes under 2.0 MPa to yield MEA by peeling only the polytetrafluoroethylene sheet.

The cathode catalyst layer transcribed on the solid polymer electrolyte membrane had a thickness of about 12 μm, a Pt supporting amount of 0.35 mg per apparent electrode surface area of 1 cm^2, and an electrode area of 25 cm^2. The anode catalyst layer had a thickness of about 1.5 μm, a Pt supporting amount of 0.05 mg per apparent electrode surface area of 1 cm^2, and an electrode area of 25 cm^2.

6. Performance evaluation of a membrane-electrode assembly (MEA)

At the both sides of the resultant MEA, carbon paper (a size of 6.0 cm ×5.5 cm, and a thickness of 320 μm) as the gas diffusion layer, and a gas separator with a gas flow channel were arranged, and further it was sandwiched with power collecting plates made of gold plated stainless steel to prepare a unit cell for evaluation. To the anode side of the unit cell for evaluation was supplied hydrogen as fuel, and to the cathode side thereof was supplied air as an oxidizing agent. Supplying pressure of both gases was set to atmospheric pressure, and hydrogen was set to be 58.6°C and a relative humidity of 60%, and air to be 54.8°C and a relative humidity of 50%, and cell temperature was set at 70°C. In addition, utilization rate of hydrogen was set to be 67%, and utilization rate of air was set to be 40%. Cell voltage measured in power generation at a current density of 1.0 A/cm^2 under these conditions, was used as initial stage cell voltage.

[0073] Subsequently, after 60 seconds of power generation, power generation was stopped. After the stopping, supplying of hydrogen and air was also stopped and the cell was purged with air and stood still for 50 seconds. Then, hydrogen gas was supplied to the anode side for 10 seconds at 1/5 of the utilization rate. Then, hydrogen gas and air were supplied to the anode side and the cathode side, respectively under the similar condition as in the above, and again power generation was continued for 60 minutes under a current density of 1.0 A/cm^2. In addition, load current here was increased from 0 A/cm^2 to 1 A/cm^2 taking 30 seconds. After carrying out this power generation-stop operation, cell voltage was measured to evaluate power generation performance. Cycle number till cell voltage became 0.45 V under a current density of 1.0 A/cm^2 was used as evaluation value of durability. The compositions and results are shown in Table 1-1. In addition, heat treatment temperature in graphitization treatment, BET specific surface area, true density, lattice spacing, d $_{002}$, and electric conductivity of the conductive carbon material used in the cathode electrode catalyst are summarized in Table 4.

Working Examples 2 to 25 and Reference Examples 1 to 5

[0074] Similarly as in Working Example 1 except that compositions of fuel cells were changed as shown in Table 1-1 and Table 1-2, MEAs were prepared and durability was evaluated. Compositions and results are shown in Table 1-1 and Table 1-2. In addition, heat treatment temperature in graphitization treatment, BET specific surface area, true density, lattice spacing, d$_{002}$, and electric conductivity of the conductive carbon material used in the cathode electrode catalyst are summarized in Table 4.

Working Example 26

[0075]

1. Preparation of a cathode electrode catalyst
Similarly as in Working Example 1, the cathode electrode catalyst was prepared and this was used as the cathode electrode catalyst (C).
Then, by graphitization treatment of carbon black (Vulcan XC-72 produced from Cabot Co., Ltd.) at 2700°C for 10 hours, graphitized carbon black (graphitized Vulcan XC-72; BET surface area=113 m^2/g, true density=2.01 g/cm^3, lattice spacing, d$_{002}$, =3.46 Å, electric conductivity=300S/cm) was yielded. To 4.0 g of the graphitized carbon black, 400 g of an aqueous solution of dinitrodiamine platinum (a Pt concentration of 1.0%) was added and stirred for 1 hr. Further, 50 g of formic acid was mixed as a reducing agent and stirred for 1 hr. Subsequently, the solution was warmed to 40°C taking 30 minutes, followed by stirring at 40°C for 6 hrs, warming to 60°C taking 30 minutes, further stirring at 60°C for 6 hrs and cooling to room temperature taking 1 hr. The precipitate was filtered, and then the resultant solid substance was dried at 85°C for 12 hrs under reduced pressure, and crushed in a mortar to yield an cathode electrode catalyst (D) (an average particle diameter of Pt particles of 4.8 nm, and a Pt supporting concentration of 50% by mass).
2. Preparation of a cathode catalyst layer
Purified water of 5 times mass based on mass of the mixture obtained by mixing the electrode catalyst (C) and the electrode catalyst (D) in mass ratio (C)/(D)=2/1, was added, and subjected to defoaming operation under reduced pressure for 5 minutes. To this solution, 0.5 times mass of n-propyl alcohol was added, and further a solution containing a proton conductive polymer electrolyte (containing 20% by weight of Nafion™ produced from DuPont Co., Ltd.) was added. As content of the polymer electrolyte in the solution, one having mass ratio of solid content to the mass of carbon of the mixture (the electrode catalyst (C) and (D)), Carbon/ Ionomer =1.0/0.9, was used. The resultant mixture slurry was sufficiently dispersed by an ultrasonic homogenizer and subjected to defoaming operation under reduced pressure to yield catalyst slurry.

[0076] Similarly as in Working Example 1, except by using the above catalyst slurry, the cathode catalyst layer was prepared at the one surface of the polytetrafluoroethylene sheet, to yield MEA using thereof and evaluated. Compositions and results are shown in Table 2. In addition, heat treatment temperature in graphitization treatment, BET specific surface area, true density, lattice spacing, d $_{002}$, and electric conductivity of the conductive carbon material used in the

Table 1-2

	Anode electrode catalyst type	Cathode Electrode catalyst type	Supported catalyst amount (mg/cm^2)		Anode Catalyst layer Average Thickness Ya (μm)	cathode catalyst layer Average thickness Yc (μm)	Ya/Yc (-)	GDL Thickness (μm)	Start-stop times (time)
	Catalyst CCM	Catalyst CCM	A	C					
Work Exl 15	Pt 50wt% % GKB EC	Pt 50wt% GKB EC	0.05	0.35	2.5	12.0	0.21	320	3,740
Work Exl 16	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.05	0.35	2.5	12.0	0.21	320	2,830
Work Exl 17	Pt 50wt% KB EC	Pt 50wt% GBP	0.05	0.35	2.0	12.0	0.17	180	2,770
Work Exl 18	Pt 50wt% KB EC	Pt 50wt% GKB EC600JD	0.15	0.35	6.0	12.0	0.50	180	1,950
Work Exl 19	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.10	0.35	2.0	12.0	0.17	320	2,230
Work Exl 20	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.10	0.35	2.0	12.0	0.17	320	2,480
Work Exl 21	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.10	0.35	2.0	12.0	0.17	320	2,550
Work Exl 22	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.10	0.35	2.0	12.0	0.17	320	2,980
Work Exl 23	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.10	0.35	2.0	12.0	0.17	320	3,130
Work Exl 24	Pt 50wt% KB EC	Pt 50wt% GKB EC 600JD	0.10	0.35	2.0	12.0	0.17	320	2,540
Work Ex1 25	Pt 50wt% KB EC	Pt 50wt% GBP	0.10	0.35	2.0	12.0	0.17	320	2,610
Reference Ex1 1	Pt 50wt% KB EC	Pt 50wt% KB EC	0.4	0.4	13.7	13.7	1.0	320	450
Reference Exl 2	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.4	0.4	14	14	1.0	320	750
Reference Exl 3	Pt 50wt% V XC-72	Pt 50wt% GKB EC	0.4	0.4	14	14	1.0	320	730
Reference Exl 4	Pt 50wt% KB EC	Pt 50wt% GKB EC	0.4	0.2	14	7.0	2.0	320	680
Reference Exl 5	Pt 50wt% GKB EC	Pt 50wt% KB EC	0.4	0.4	14	14	1.0	320	530

(Note) Work Exl: Working Example, Exl: Example, CCM: Conductive carbon material,
A: Anode, C: Cathode,
GKB EC: Graphitized Ketjenblack EC, KB: Ketjenblack, V XC-72: Vulkan XC-72
GBP: Graphitized Black Pearls

Table 4

	CCM in CEC (Heat Treatment temp)	BET surface area (m^2/g)	True Density (g/cm^3)	$d_{00\,2}$ (Å)	Electric conductivity (S/cm)
Work Exls 1 to 16 Exls 2 to 4	GKB EC (2700°C)	130	1.93	3.51	200
Work Exl 17	GBP (2700°C)	320	1.91	3.49	250
Work Exl 18	GKB EC 600 JD (2700°C)	285	1.85	3.50	250
Work Exl 19	GKB EC (2400°C)	190	1.80	3.55	100
Work Exl 20	GKB EC (2500°C)	160	1.85	3.53	130
Work Exl 21	GKB EC (2600°C)	145	1.90	3.52	160
Work Exl 22	GKB EC (2800°C)	115	1.96	3.50	300
Work Exl 23	GKB EC (2900°C)	105	1.99	3.48	400
Work Exl 24	GKB EC 600 JD (2500°C)	270	1.81	3.53	180
Work Exl 25	GBP (2500°C)	295	1.83	3.54	190
Reference Exls 1, 5	KB EC	800	1.80	-	20
(Note) Work Exl: Working Example, Exl: Example, CCM: Conductive carbon material, CEC: Cathode electrode catalyst GKB EC: Graphitized Ketjenblack EC, GBP: Graphitized Black Pearls, KB EC: Ketjenblack EC					

Claims

1. A membrane-electrode assembly for a fuel cell comprising:

a cathode catalyst layer containing a cathode catalyst comprising platinum or a platinum alloy, a conductive carbon material supporting said cathode catalyst, and a proton conductive polymer electrolyte;
a solid polymer electrolyte membrane; and
an anode catalyst layer containing an anode catalyst, a conductive carbon material supporting said anode catalyst, and
a proton conductive polymer electrolyte; **characterized in that** the average thickness of said anode catalyst layer (Ya) is smaller than the average thickness of said cathode catalyst layer (Yc), and wherein said conductive carbon material of the cathode catalyst layer comprises graphitized carbon black.

2. The membrane-electrode assembly for a fuel cell according to claim 1, wherein said Ya and said Yc satisfy the relation of Ya/Yc=0.01 to 0.9.

3. The membrane-electrode assembly for a fuel cell according to claim 1 or 2, wherein said Ya is 0.3 to 10 μm and said Yc is 7 to 20 μm.

4. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 3, wherein said graphitized carbon black has a true density of 1.80 to 2.11 g/cm^3, a lattice spacing, d_{002}, of 3.36 to 3.55 Å and an electric conductivity of 50 to 1000 S/cm.

5. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 4, wherein said graphitized carbon black comprises graphitized carbon black (A) having a BET surface area of not smaller than 100 m^2/g.

6. The membrane-electrode assembly for a fuel cell according to claim 5, wherein the BET surface area of said carbon black (A) is 100 to 300 m^2/g.

7. The membrane-electrode assembly for a fuel cell according to claim 5 or 6, wherein the BET surface area of said carbon black (A) is 120 to 250 m^2/g and more.

8. The membrane-electrode assembly for a fuel cell according to any of claims 5 to 7, wherein said cathode catalyst is supported on said carbon black (A) to form a cathode electrode catalyst (C), and the amount of said supported cathode catalyst in said cathode electrode catalyst (C) is 20 to 80% by mass.

9. The membrane-electrode assembly for a fuel cell according to any one of claims 1 to 8, wherein said graphitized carbon black further comprises graphitized carbon black (B) having a BET surface area of smaller than 100 m^2/g.

10. The membrane-electrode assembly for a fuel cell according to claim 9, wherein the BET surface area of said carbon black (B) is 80 to 100 m^2/g.

11. The membrane-electrode assembly for a fuel cell according to claim 9 or 10, wherein said cathode catalyst is supported on said carbon black (B) to form a cathode electrode catalyst (D), and the amount of said supported cathode catalyst in said cathode electrode catalyst (D) is 10 to 50% by mass.

12. The membrane-electrode assembly for a fuel cell according to any of claims 9 to 11, wherein mixing ratio of said cathode electrode catalyst (C) and said cathode electrode catalyst (D) is not smaller than 60/40 in mass ratio ((C)/(D)).

13. The membrane-electrode assembly for a fuel cell according to claim 12, wherein mixing ratio of said cathode electrode catalyst (C) and said cathode electrode catalyst (D) is 60/40 to 99/1 in mass ratio ((C)/(D)).

14. The membrane-electrode assembly for a fuel cell according to claim 12 or 13, wherein ratio of mixing ratio (R_{up}) between said cathode electrode catalyst (C) and said cathode electrode catalyst (D) at the upstream side of the gas flow channel of said cathode catalyst layer, and mixing ratio (R_{down}) between said cathode electrode catalyst (C) and said cathode electrode catalyst (D) at the downstream side of the gas flow channel of said cathode catalyst layer is not smaller than 1/1.

15. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 14, wherein said conductive carbon material of the cathode catalyst layer further comprises hydrophobicity-treated carbon black to be hydrophobized using a fluorine compound in an amount of 1 to 20% by mass based on total mass of the conductive carbon material of said cathode catalyst layer.

16. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 15, wherein said conductive carbon material of the cathode catalyst layer further comprises a carbon nanotube, a carbon nanofiber or a carbon nanohorn in an amount of 1 to 20% by mass based on total mass of the conductive carbon material of said cathode catalyst layer.

17. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 16, wherein said platinum alloy is an alloy between at least one base metal selected among chromium, manganese, iron, cobalt and nickel, and platinum.

18. The membrane-electrode assembly for a fuel cell according to claim 17, wherein mixing ratio of said platinum and said base metal in said platinum alloy is 1/1 to 5/1 in mass ratio (platinum/base metal).

19. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 18, wherein said conductive carbon material of the anode catalyst layer comprises carbon black.

20. The membrane-electrode assembly for a fuel cell according to claim 19, wherein said conductive carbon material of the anode catalyst layer comprises graphitized carbon black.

21. The membrane-electrode assembly for a fuel cell according to any of claims 1 to 20, wherein said anode catalyst is supported on said conductive carbon material to form an anode electrode catalyst, and the amount of said supported anode catalyst in said anode electrode catalyst is 30 to 70% by mass.

22. The membrane-electrode assembly for a fuel cell according to any one of claims 1 to 21, wherein a gas diffusion layer with a thickness of not thicker than 200 μm, composed of a water-repellent treated carbon paper, is arranged at the outsides of said cathode catalyst layer and said anode catalyst layer.

23. The membrane-electrode assembly for a fuel cell according to claim 22, wherein a mil layer is arranged between said gas diffusion layer, and said cathode catalyst layer and said anode catalyst layer.

24. A proton-exchange membrane fuel cell **characterized by** the use of the membrane-electrode assembly for a fuel cell set forth in any one of claims 1 to 23.

25. A vehicle mounted with the proton-exchange membrane fuel cell set forth in claim 24.

Patentansprüche

1. Membran-Elektroden-Anordnung für eine Brennstoffzelle, umfassend:

eine Kathoden-Katalysatorschicht mit einem Kathodenkatalysator, der Platin oder eine Platinlegierung umfasst, einem leitfähigen Kohlenstoffmaterial, das den Kathodenkatalysator trägt, und einem protonenleitenden Polymerelektrolyt;
eine feste Polymerelektrolytmembran; und
eine Anoden-Katalysatorschicht mit einem Anodenkatalysator, einem leitfähigen Kohlenstoffmaterial, das den Anodenkatalysator trägt, und einem protonenleitenden Polymerelektrolyt; **dadurch gekennzeichnet, dass** die durchschnittliche Dicke der Anoden-Katalysatorschicht (Ya) geringer als die durchschnittliche Dicke der Kathoden-Katalysatorschicht (Yc) ist, und wobei das leitfähige Kohlenstoffmaterial der Kathoden-Katalysatorschicht graphitisiertes Carbon Black aufweist.

2. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 1, wobei Ya und Yc die Gleichung Ya/Yc = 0,01 bis 0,9 erfüllen.

3. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 1 oder 2, wobei Ya 0,3 bis 10 μm und Yc 7 bis 20 μm betragen.

4. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 3, wobei das graphitisierte Carbon Black eine wahre Dichte von 1,80 bis 2,11 g/cm^3, einen Gitterabstand, d_{002}, von 3,36 bis 3,55 Å und eine elektrische Leitfähigkeit von 50 bis 1000 S/cm aufweist.

5. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 4, wobei das graphitisierte Carbon Black graphitisiertes Carbon Black (A) mit einem BET-Oberflächenbereich von nicht weniger als 100 m^2/g umfasst.

6. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 5, wobei der BET-Oberflächenbereich des Carbon Black (A) 100 bis 300 m^2/g beträgt.

7. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 5 oder 6, wobei der BET-Oberflächenbereich des Carbon Black (A) 120 bis 250 m^2/g beträgt.

8. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 5 bis 7, wobei der Kathodenkatalysator auf dem Carbon Black (A) gelagert ist, um einen Kathoden-Elektrodenkatalysator (C) zu bilden, und die Menge des gelagerten Kathodenkatalysators in dem Kathoden-Elektrodenkatalysator (C) 20 bis 80 Masse% beträgt.

9. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 8, wobei das graphitisierte Carbon Black ferner graphitisiertes Carbon Black (B) mit einem BET-Oberflächenbereich kleiner als 100 m^2/g umfasst.

10. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 9, wobei der BET-Oberflächenbereich des Carbon Black (B) nicht weniger als 80 m^2/g und weniger als 100 m^2/g beträgt.

11. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 9 oder 10, wobei der Kathodenkatalysator auf dem Carbon Black (B) gelagert ist, um einen Kathoden-Elektrodenkatalysator (D) zu bilden, und die Menge des gelagerten Kathodenkatalysators in dem Kathoden-Elektrodenkatalysator (D) 10 bis 50 Masse% beträgt.

12. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 9 bis 11, wobei das Mischverhältnis des Kathoden-Elektrodenkatalysators (C) und des Kathoden-Elektrodenkatalysators (D) nicht kleiner als 60/40 im Masseverhältnis ((C)/(D)) ist.

13. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 12, wobei das Mischverhältnis des Kathoden-Elektrodenkatalysators (C) und des Kathoden-Elektrodenkatalysators (D) 60/40 bis 99/1 im Masseverhältnis ((C)/(D)) ist.

14. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 12 oder 13, wobei das Mischverhältnis (R_{up}) zwischen dem Kathoden-Elektrodenkatalysator (C) und dem Kathoden-Elektrodenkatalysator (D) an der stromaufwärtsseitigen Seite des Gasdurchflusskanals der Kathoden-Katalysatorschicht und das Mischverhältnis (R_{down}) zwischen dem Kathoden-Elektrodenkatalysator (C) und dem Kathoden-Elektrodenkatalysator (D) an der stromabwärtsseitigen Seite des Gasdurchflusskanals der Kathoden-Katalysatorschicht nicht kleiner als 1/1 ist.

15. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 14, wobei das leitfähige Kohlenstoffmaterial der Kathoden-Katalysatorschicht ferner ein hydrophob behandeltes Carbon Black umfasst, das unter Verwendung einer Fluorzusammensetzung in einer Menge von 1 bis 20 Masse% basierend auf der Gesamtmasse des leitfähigen Kohlenstoffmaterials der Kathoden-Katalysatorschicht hydrophob gemacht werden soll.

16. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 15, wobei das leitfähige Kohlenstoffmaterial der Kathoden-Katalysatorschicht ferner ein Kohlenstoffnanoröhrchen, eine Kohlenstoffnanofaser oder ein Kohlenstoffnanohorn in einer Menge von 1 bis 20 Masse% basierend auf der Gesamtmasse des leitfähigen Kohlenstoffmaterials der Kathoden-Katalysatorschicht umfasst.

17. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 16, wobei die Platinlegierung eine Legierung aus zumindest einem Basismetall, ausgewählt aus Chrom, Mangan, Eisen, Kobalt und Nickel, und Platin ist.

18. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 17, wobei das Mischverhältnis des Platins und des Basismetalls in der Platinlegierung 1/1 bis 5/1 im Masseverhältnis (Platin/Basismetall) ist.

19. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 18, wobei das leitfähige Kohlenstoffmaterial der Anoden-Katalysatorschicht Carbon Black umfasst.

20. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 19, wobei das leitfähige Kohlenstoffmaterial der Anoden-Katalysatorschicht graphitisiertes Carbon Black umfasst.

21. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 20, wobei der Anodenkatalysator auf dem leitfähigen Kohlenstoffmaterial gelagert ist, um einen Anoden-Elektrodenkatalysator zu bilden, und die Menge des gelagerten Anodenkatalysators in dem Anoden-Elektrodenkatalysator 30 bis 70 Masse% beträgt.

22. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 21, wobei eine Gasdiffusionsschicht mit einer Dicke von nicht mehr als 200 μm, bestehend aus einem mit einem wasserabstoßenden Stoff behandelten Kohlenstoffpapier, an den Außenseiten der Kathoden-Katalysatorschicht und der Anoden-Katalysatorschicht angeordnet ist.

23. Membran-Elektroden-Anordnung für eine Brennstoffzelle nach Anspruch 22, wobei eine Millimeterschicht zwischen der Gasdiffusionsschicht und der Kathoden-Katalysatorschicht sowie der Anoden-Katalysatorschicht angeordnet ist.

24. Protonenaustauschmembran-Brennstoffzelle, **gekennzeichnet durch** die Verwendung der Membran-Elektroden-Anordnung für eine Brennstoffzelle nach einem der Ansprüche 1 bis 23.

25. Fahrzeug mit der Protonenaustauschmembran-Brennstoffzelle nach Anspruch 24.

Revendications

1. Ensemble membrane-électrodes pour une pile à combustible qui comprend :

une couche de catalyseur de cathode contenant un catalyseur de cathode comprenant du platine ou un alliage de platine, un matériau conducteur à base de carbone supportant ledit catalyseur de cathode, et un électrolyte polymère conducteur de protons ;
une membrane d'électrolyte polymère solide ; et
une couche de catalyseur d'anode contenant un catalyseur d'anode, un matériau conducteur à base de carbone supportant ledit catalyseur d'anode, et un électrolyte polymère conducteur de protons ; **caractérisé en ce que** l'épaisseur moyenne de ladite couche de catalyseur d'anode (Ya) est plus petite que l'épaisseur moyenne de ladite couche de catalyseur de cathode (Yc), et dans lequel ledit matériau conducteur à base de carbone de la couche de catalyseur de cathode comprend du noir de carbone graphitisé.

2. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 1, dans lequel ladite Ya et ladite Yc satisfont la relation Ya/Yc = 0,01 à 0,9.

3. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 1 ou 2, dans lequel ladite Ya est de 0,3 à 10 μm et ladite Yc est de 7 à 20 μm.

4. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 3, dans lequel ledit noir de carbone graphitisé a une masse volumique réelle allant de 1,80 à 2,11 g/cm^3, une constante réticulaire, d_{002}, allant de 3,36 à 3,55 Å et une conductivité électrique allant de 50 à 1000 S/cm.

5. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 4, dans lequel ledit noir de carbone graphitisé comprend du noir de carbone graphitisé (A) ayant une surface BET qui n'est pas inférieure à 100 m^2/g.

6. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 5, dans lequel la surface BET dudit noir de carbone (A) est de 100 à 300 m^2/g.

7. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 5 ou 6, dans lequel la surface BET dudit noir de carbone (A) est de 120 à 250 m^2/g et plus.

8. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 5 à 7, dans lequel ledit catalyseur de cathode est supporté sur ledit noir de carbone (A) pour former un catalyseur d'électrode cathodique (C), et la quantité dudit catalyseur de cathode supporté dans ledit catalyseur d'électrode cathodique (C) est de 20 à 80% en masse.

9. Ensemble membrane-électrodes pour une pile à combustible selon l'une quelconque des revendications 1 à 8, dans lequel ledit noir de carbone graphitisé comprend en outre du noir de carbone graphitisé (B) ayant une surface BET inférieure à 100 m^2/g.

10. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 9, dans lequel la surface BET dudit noir de carbone (B) est de 80 à 100 m^2/g.

11. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 9 ou 10, dans lequel ledit catalyseur de cathode est supporté sur ledit noir de carbone (B) pour former un catalyseur d'électrode cathodique (D), et la quantité dudit catalyseur de cathode supporté dans ledit catalyseur d'électrode cathodique (D) est de 10 à 50% en masse.

12. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 9 à 11, dans lequel le rapport de mélange entre ledit catalyseur d'électrode cathodique (C) et ledit catalyseur d'électrode cathodique (D) n'est pas inférieur à 60/40 en rapport massique ((C)/(D)).

13. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 12, dans lequel le rapport de mélange entre ledit catalyseur d'électrode cathodique (C) et ledit catalyseur d'électrode cathodique (D) est de 60/40 à 99/1 en rapport massique ((C)/(D)).

14. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 12 ou 13, dans lequel le rapport entre le rapport de mélange (R_{up}) entre ledit catalyseur d'électrode cathodique (C) et ledit catalyseur d'électrode cathodique (D) au niveau du côté amont du canal d'écoulement de gaz de ladite couche de catalyseur de cathode, et le rapport de mélange (R_{down}) entre ledit catalyseur d'électrode cathodique (C) et ledit catalyseur d'électrode cathodique (D) au niveau du côté aval du canal d'écoulement de gaz de ladite couche de catalyseur de cathode n'est pas inférieur à 1/1.

15. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 14, dans lequel ledit matériau conducteur à base de carbone de la couche de catalyseur de cathode comprend en outre du noir de carbone rendu hydrophobe par un traitement utilisant un composé fluoré en une quantité allant de 1 à 20% en masse sur la base de la masse totale du matériau conducteur à base de carbone de ladite couche de catalyseur de cathode.

16. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 15, dans lequel ledit matériau conducteur à base de carbone de la couche de catalyseur de cathode comprend en outre un nanotube de carbone, une nanofibre de carbone ou un nanocornet de carbone en une quantité allant de 1 à 20% en masse sur la base de la masse totale du matériau conducteur à base de carbone de ladite couche de catalyseur de cathode.

17. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 16, dans lequel ledit alliage de platine est un alliage entre au moins un métal de base choisi parmi le chrome, le manganèse, le fer, le cobalt et le nickel, et le platine.

18. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 17, dans lequel le rapport de mélange entre ledit platine et ledit métal de base dans ledit alliage de platine est de 1/1 à 5/1 en rapport massique (platine/métal de base).

19. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 18, dans lequel ledit matériau conducteur à base de carbone de la couche de catalyseur d'anode comprend du noir de carbone.

20. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 19, dans lequel ledit matériau conducteur à base de carbone de la couche de catalyseur d'anode comprend du noir de carbone graphitisé.

21. Ensemble membrane-électrodes pour une pile à combustible selon l'une des revendications 1 à 20, dans lequel ledit catalyseur d'anode est supporté sur ledit matériau conducteur à base de carbone pour former un catalyseur d'électrode anodique, et la quantité dudit catalyseur d'anode supporté dans ledit catalyseur d'électrode anodique est de 30 à 70% en masse.

22. Ensemble membrane-électrodes pour une pile à combustible selon l'une quelconque des revendications 1 à 21, dans lequel une couche de diffusion de gaz ayant une épaisseur qui n'est pas supérieure à 200 μm, composée d'un papier de carbone rendu hydrofuge par un traitement, est agencée à l'extérieur de ladite couche de catalyseur de cathode et de ladite couche de catalyseur d'anode.

23. Ensemble membrane-électrodes pour une pile à combustible selon la revendication 22, dans lequel une couche d'un mil est agencée entre ladite couche de diffusion de gaz, et ladite couche de catalyseur de cathode et ladite couche de catalyseur d'anode.

24. Pile à combustible à membrane échangeuse de protons **caractérisée par** l'utilisation de l'ensemble membrane-électrodes pour une pile à combustible selon l'une quelconque des revendications 1 à 23.

25. Véhicule dans lequel est montée la pile à combustible à membrane échangeuse de protons selon la revendication 24.

REFERENCES CITED IN THE DESCRIPTION

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